Materials and Components for Fuel Cell Stacks

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AGENDA

- Introduction of Fuel Cell
- Fuel Cell vs. Battery
- Fuel Cell Types
- Major Components in Fuel Cell
- What is MEA?
- How to Fabricate MEAs?
- Some Important Reactions
- Membranes, Catalysts, Flow Fields

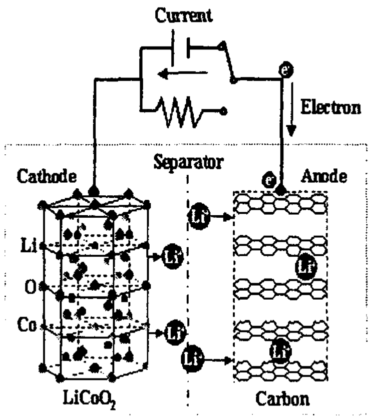
WHAT IS FUEL CELL?

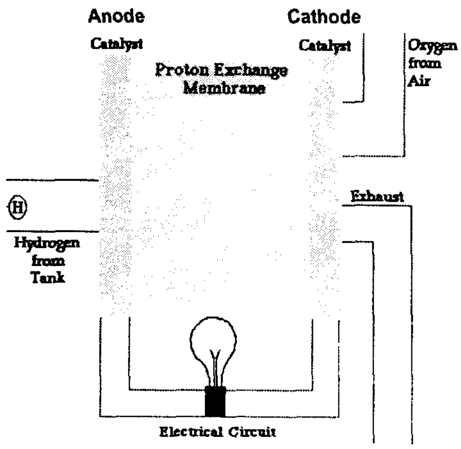
- A fuel cell is an electrochemical device, which converts chemical energy of hydrogen or methanol to electrical energy without combustion. Unlike a battery, a fuel cell will continuously produce electricity as long as fuel is supplied to it.

WHY FUEL CELL?

- High energy efficiency-35% to 75%
- No environmental intrusion
  Products: Hot water, CO_2, < 1 ppm No_x, < 10 ppm CO
- Direct energy conversion (no combustion)
- No moving parts in the energy converter
- Fuel flexibility
- Demonstrated endurance/reliability of lower temperature units
- Remote/unattended operation
- Size flexibility
- Rapid load following capability

FUEL CELL VS. BATTERY





FUEL CELL VS. BATTERY

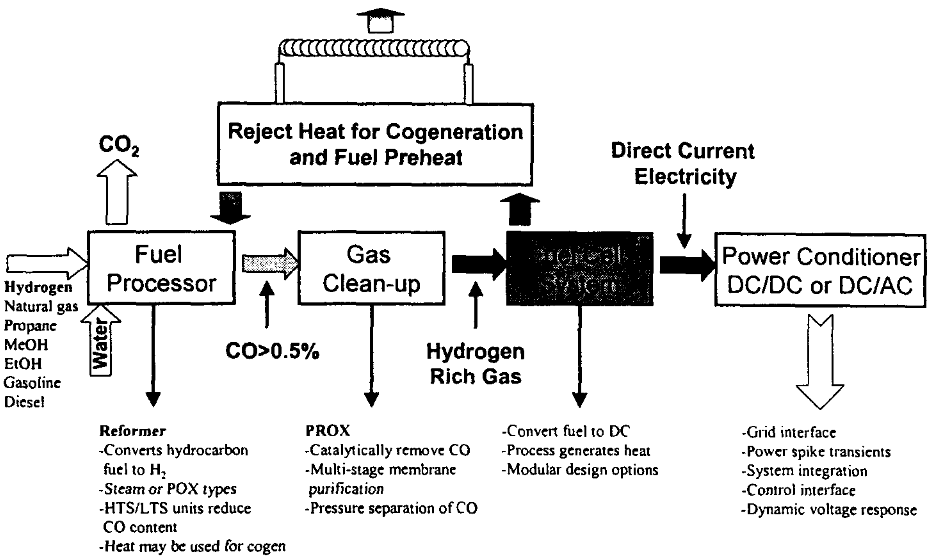
Cell Type	E (V)	i (mA/cm^2)	Specific Energy (Wh/kg)	Energy Density (Wh/l)
Ni/Cd	1.2	0.1	70	200
Ni/MH	1.2	0.1	90	320
Li/$LiCoO_2$	3.7	0.1	150	400
CH_3OH/O_2 DMFC	0.4	400	Min 320 (3450^c)	686^b (3000^c)
H_2/Air PEMFC	0.7	600	100 ($33,288^*$)	765^*

*Energy density of based on compressed hydrogen (34.5 Mpa)
[b]Saturated fuel at 0.5V
[c]Fuel energy density in 1:1 molar ratio with water
•3.6kW/l for gasoline engine, 1.4kW/l for diesel engine, 1.0kW/l for PEMFC, KRI (1997)

FUEL CELL TYPES

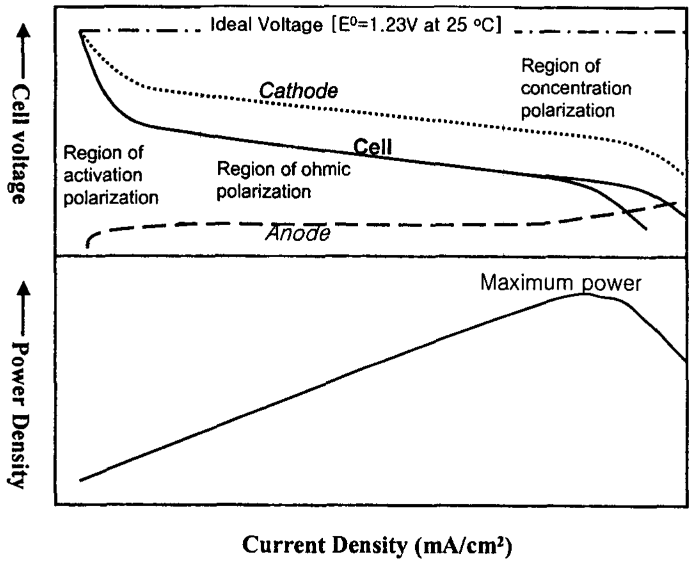
	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Ionic polymer	KOH	H_3PO_4/SiC	$Li_2CO_3+K_2CO_3$/ γ-$LiAlO_2$	YSZ
Temp.	80~95 ℃	65-220 ℃	180~210 ℃	600~700 ℃	800~1000 ℃
Charge carri	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Plate	Graphite	Graphite	Glassy Carbon	Stainless Steel	La(Sr)CrO_3
Catalyst (A/C	Pt/Pt	Pt	Pt	Ni-Cr/Lithiated NiO	La(Sr)MnO_3
Anode Reaction	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode Reaction	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$1/2O_2 + 2e^- \rightarrow O^{2-}$
Realized Power	1-250 kW	5-150 kW	50 kW-11 MW	100 kW-2 MW	100-250 kW
CO Gas	Poison (<50 ppm)	Poison	Poison (<0.5%)	Fuel	Fuel

BASIC FUEL CELL SYSTEM



POX: Partial oxidation
PROX: Preferential oxidation

I/V CHARACTERISTICS

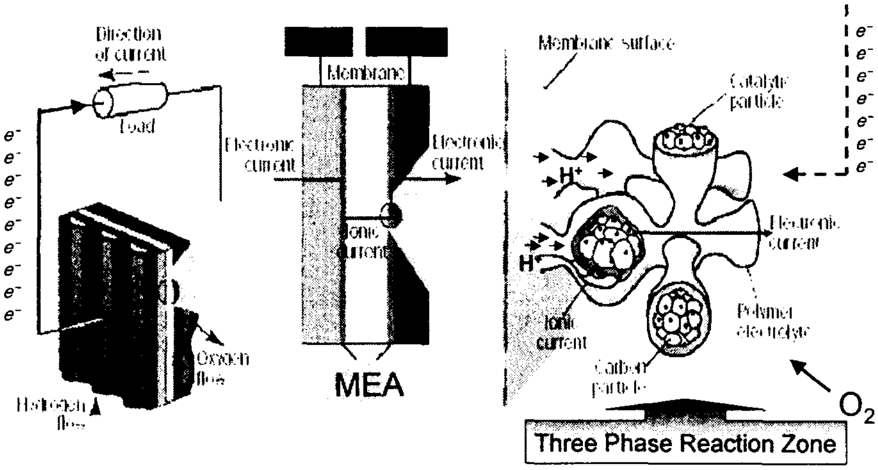


MAJOR COMPONENTS OF FUEL CELL

Stack

- **MEA**
  - Membrane
  - Catalyst
  - Catalyst support
  - Gas diffusion layer
  - Gaskets/frames
- **Bipolar plate**
  - Flow field
  - Separator/connector
- Bus plates/terminals
- End plates
- Clamping mechanism
- Fluid connections
- Manifolds
- Cooling plates/arrangements
- Humidification section (optional)

WHAT IS MEA?



$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

HOW TO FABRICATE MEA?

- Spray coating
- Decal
- Tape casting
- Screen printing-plain
- Physical Vapor Deposition-sputtering
- Roll coating-screen printing, power scattering
- Flexographic printing, gravure printing

IMPORTANT REACTIONS

1. Hydrogen oxidation
2. Methanol oxidation
3. Oxygen reduction

$H_2 \rightarrow 2H^+ + 2e^-,\ E^o = 0\ V$

$$2\,Pt_{(s)} + H_2 \rightarrow Pt - H_{ads} + Pt - H_{ads}$$

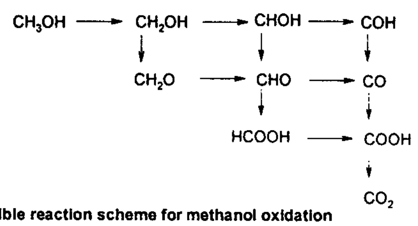
$$Pt - H_{ads} \rightarrow H^+ + e^- + Pt_{(s)}$$

where $Pt_{(s)}$ is a free surface site and $Pt - H_{ads}$ is an adsorbed H - atom on the Pt active site.

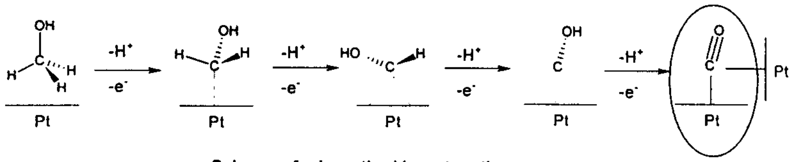
IMPORTANT REACTIONS

1. Hydrogen oxidation
2. Methanol oxidation
3. Oxygen reduction

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-, E^0 = 0.046V$



Possible reaction scheme for methanol oxidation



Scheme of adsorption/deprotonation process

IMPORTANT REACTIONS

1. Hydrogen oxidation
2. Methanol oxidation
3. Oxygen reduction

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-, E^0 = 0.046V$$

Water gas shift reaction

0.7V

$$Pt + H_2O \rightarrow PtOH + H^+ + 1e^- \quad + \quad PtCO \quad = 2Pt + CO_2 + H^+ + 1e^-$$

0.2V

$$Ru + H_2O \rightarrow RuOH + H^+ + 1e^- \quad + \quad PtCO \quad = Ru + Pt + CO_2 + H^+ + 1e^-$$

IMPORTANT REACTIONS

1. Hydrogen oxidation
2. Methanol oxidation
3. Oxygen reduction

$$1/2\,O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$O_2 + Pt \rightarrow Pt-O_2$$

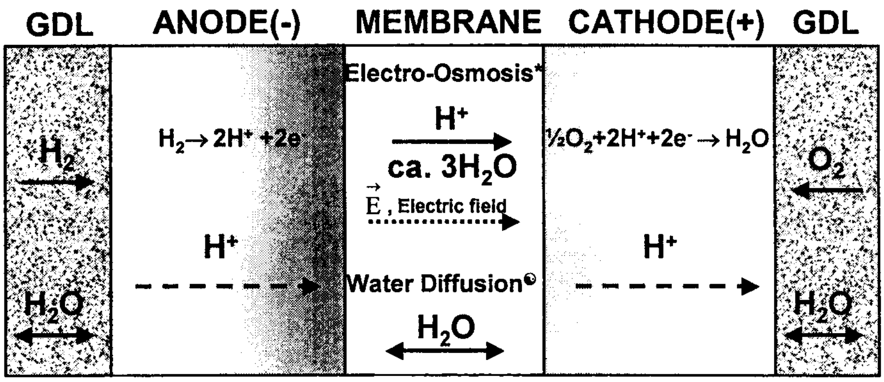
$$Pt-O_2 + H^+ + 1e^- \rightarrow Pt-HO_2$$

$$Pt-HO_2 + Pt \xrightarrow{rds} Pt-OH + Pt-O$$

$$Pt-OH + Pt-O + 3H^+ + 3e^- \rightarrow 2Pt + 2H_2O$$

TRANSPORT MODES IN MEA

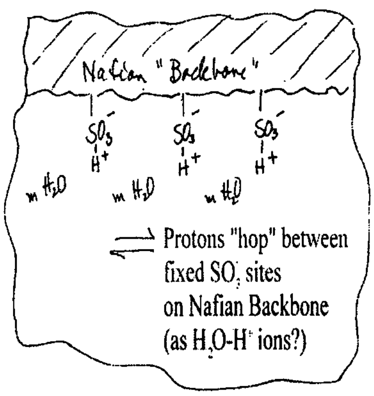
GDL:Gas Diffusion Layer,
Carbon paper or cloth



$*N_{\text{Water flux due to drag}} = I\xi(\lambda)/F$
$\xi(\lambda)$ is the electro-osmotic drag coefficient

© $N_{W,\,Diff.} = -D(\lambda)\Delta c/\,\Delta z$,
$N_{W,\,Hyd} = -k_{hyd}(\lambda)\Delta P/\,\Delta z$

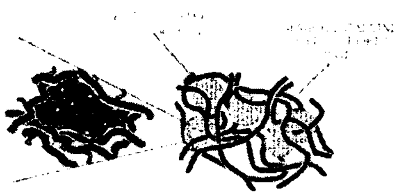
UNDERSTANDING OF PROTON CONDUCTION



- λ~2-3 ; Hydronium ions move via vehicle mechanism
- λ~4-14 ; Water in interfacial region screens weakly bound water from ion-dipole interactions
- λ>14 ; Water and protons move more freely

$\lambda(=N(H_2O)/N(SO_3H)$

ION EXCHANGE MEMBRANES



➤ REQUIREMENTS

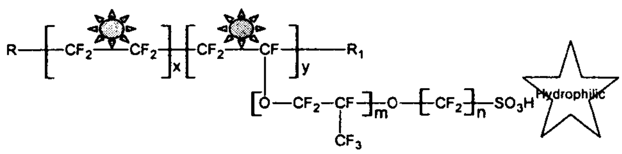
- High proton conductivity
- High/low water permeability
- Low electro-osmotic drag
- Fuel and oxygen barrier
- Chemical stability
- Mechanical and dimensional stability

⇩

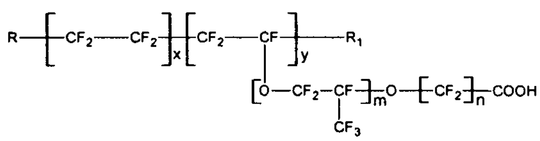
Hydrophilic (ionic) channel in hydrophobic matrix

ION EXCHANGE MEMBRANES

➤ **Perfluoriated Ionomer Membranes**



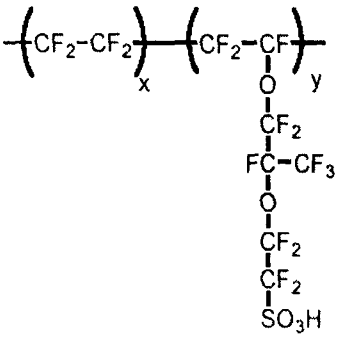
Nafion 117 (DuPont)	m>1, n=2, x=5-13, y=1
Dow XUS (Dow)	m=0, n=2, x=3-10, y=1
Flemion (Asahi Glass)	m=1, n=1-5



Aciplex (Asahi Chemical)	m=1, n=2, x=6-8, y=0-1

NAFION

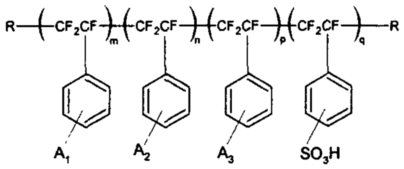
PerFluoroSulfonate Ionomer (PFSI)
e.g. Nafion®



- Copolymer of tetrafluoroethylene and perfluorinated vinylethersulfonylfluoride
- High ionic conductivity : 0.1 S/cm
- High water transport rate :2×10^5 cm^2/s
- Low voltage loss : 50 mV at $1A/cm^2$
- Low gas permeability
- Excellent long term stability

ION EXCHANGE MEMBRANES

- **Perfluoriated Ionomer Composite Membranes**
  - Incorporation of highly porous SiO_2 particles in Nafion; increase of water uptake → high temp.
  - Hydrolysis of TEOS, $Zr(OBu)_4$ in Nafion
  - Nafion with heteroolyacids (silicotungstic, phosphotungstic acids); increase of ionic conductivity
- **Partially Fluoriated Ionomer Membranes**

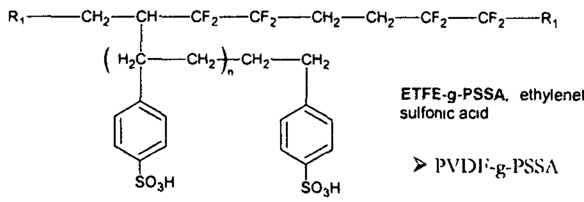


BAM based on sulfonated α,β,β -trifluorostyrene-co-substituted-α,β,β -trifluorostyrenes

at least m=2, n,p,q are integers>0

A_1, A_2, A_3=alkyls, halogens, O-R, $CF=CF_2$, CN, NO_2, OH

ION EXCHANGE MEMBRANES



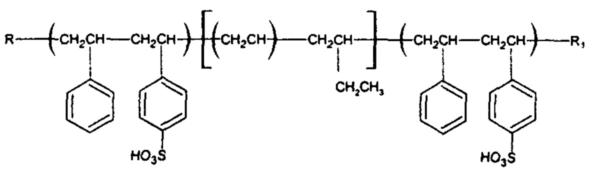
ETFE-g-PSSA, ethylenetetrafluoroethylene-g-polystyrene sulfonic acid

- PVDF-g-PSSA

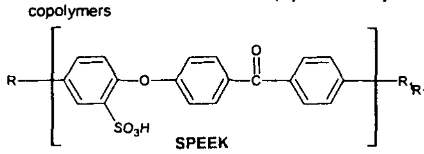
- **Partially Sulfonated Arylene Membranes (Non-fluorinated Ionomer)**
  - Sulfonation of thermally stable aromatic polymers
  - PEEK, PSf, PES, PI, PBI, PEI, PPS etc.
  - Styrene-co-ethylene-butadiene-co-styrene triblock copolymer
  - Their composites with inorganics

- **Polymer with Low MW Compounds**
  - e.g., PBI with phosphoric acid or sulfuric acid
  - Sulfonated PEEK with amphoteric compounds such as imidazole or pyrazole

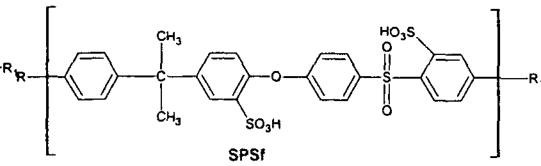
ION EXCHANGE MEMBRANES



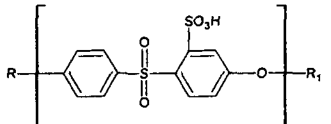
DAIS based on sulfonated SEBS (styrene-co-ethylene-butylene-co-styrene) triblock copolymers



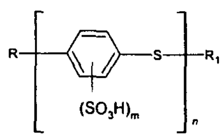
SPEEK



SPSf



SPES



Sulfonated Poly(phenylene sulfide)

WATER ISSUES OF MEMBRANES

- Humidification required
  - ♦>~80 %RH
  - ♦water management system : FC system cost ↑
- Dimensional changes in membrane with water content
  - ♦stresses at electrode/membrane interface and at the gasket
  - ♦electrode debonding from membrane
  - ♦buckling and cracking of carbon paper from shrinking membrane
- Electro-Osmotic drag (EOD)
  - ♦EOD increases with increasing T and water content
  - ♦anode humidification
  - ♦low DMFC system efficiency
- Poor dynamic response of stack
- Need for faster diffusion of cathode water back to anode ⇒ thinner membrane
  - ♦manufacturing, fuel permeation, lifetime problem

How about conductivity without water?

HIGH TEMPERATURE OPERATION

In PEMFC, it means 100-200 °C rather than 60-80 °C

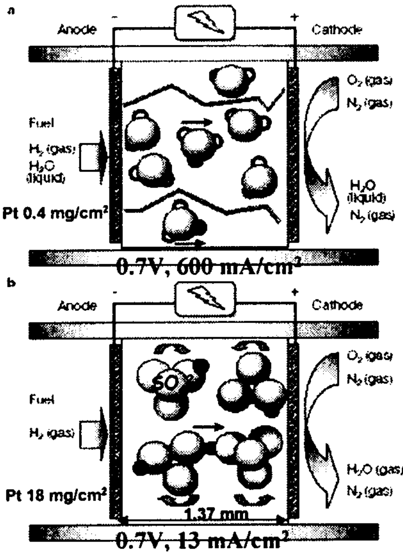
Advantages

- Better anode kinetics in the presence of CO
  - -Much simplified fuel processor
  - -Reduction in anode Pt content
- Small heat exchanger
  - -Utilizing stack heat
  - -Rejecting stack heat
- Potential to eliminate water management system ⇒ many benefits

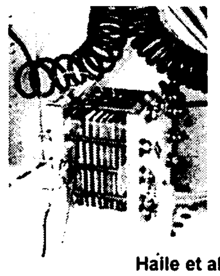
Nafion for HT

- Near-saturated water for conductivity
- Vapor pressure of water increase : 80 °C (7 psi) ⇒ 150 °C (69 psi)
- FC in high vapor pressure condition is unattractive : air compressors and water condensers
- Very short lifetime reported for fluoro ionomer at high temperature with high RH

HIGH TEMPERATURE MEMBRANES



- Candidates : Liquid electrolyte (H_3PO_4), PBI with H_3PO_4, Composite Nafion (SiO_2, $Zr(HPO_4)_2$
- Solid state electrolyte (Nature, 410(2001), 877 or 910) : create fuel cell using $CsHSO_4$ operating at 150-200 °C, but mechanically weak, sulfur reduction



Haile et al, CalTech

LIFETIME OF MEMBRANES

- All membranes have lifetime issues
- Generally PFSA is better than aromatics in FC environment
- Thermal stability
  - -C-S bond homolysis for sulfonated aromatics
- Oxidative stability
  - - Free radical generated

Polym. Deg. Stability, 67(2000), 335

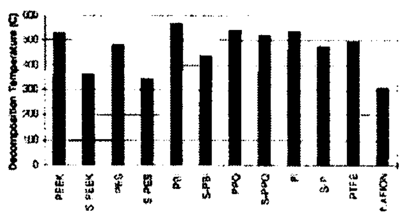


Fig. 3. Temperature of 5% weight loss in helium

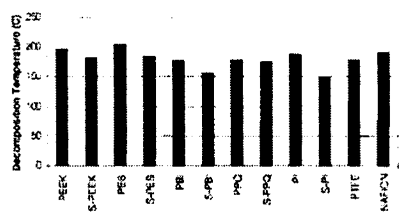


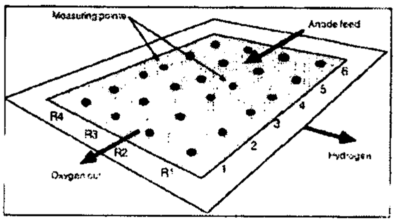
Fig. 4. Temperature of 5% weight loss in saturated vapor for 24 h.

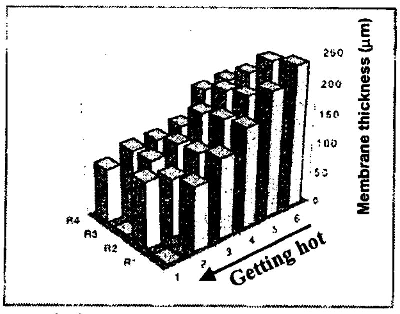
LIFETIME OF MEMBRANES

- ABB Membrel PEM electrolyser operated by SWB GmbH
- 1.7 year operation at 400 A, 80 °C

  -Pt catalyst on hydrogen side (cathode)

  -Ru/Ir catalyst on oxygen side (anode)
- Nafion shows >50% thickness loss
- $-SO_3H$ lost at same rate as thickness
- Fluoride detected in water effluent
- Erosion of membrane from hydrogen electrode side
- Most thinning near oxygen output end





J. Appl. Elect., 28(1998), 1041

ELECTRODE/MEMBRANE INTERFACE

- Traditionally, Nafion utilized as a binder and an ion conductor in MEA preparation

  -Forms three phase interface to Nafion membrane

  -Ionic contact resistance minimal
- New sulfonated aromatic membranes

  -High ionic contact resistance between Nafion based electrodes and aromatic membranes

  -Desirable for the electrode ion-conductor be the same as the membrane? ⇒ New catalyst ink formulation must be developed
- However, PBI/H_3PO_4 is good O_2 barrier : Do not use in cathode
- Desirable for the membrane surfaces be compatible with catalyst binder/electrodes

DMFC & METHANOL CROSSOVER

- Advantages over PEMFC
  - Simpler than a reformer system
  - Good thermal control of stack
  - Simpler stack design
  - Lower temperature operation compared to a reformer
  - Capable of ambient temperature start-up
  - Higher potential in terms of power density compared to the energy density of DMFC

- Implications of Methanol Crossover
  - Parasitic fuel loss; 20%
  - Lower cell voltage by 0.1V
  - Increased Air demand, polarizing cathode
  - Reduction of efficiency

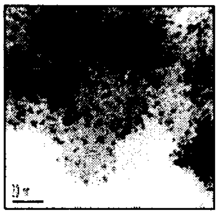
$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$

CATALYST

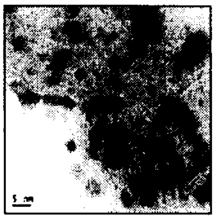
- Catalyst
  - Anode (oxidation of H_2 or CH_3OH) : Pt/C (0.1-3 mg/cm²) for PEM, Pt-Ru/C (1-4 mg/cm²) for DM
  - Cathode (reduction of O_2) : Pt/C

- Catalyst formulation
  - Wet
  - Slurry
  - Dry

TEM



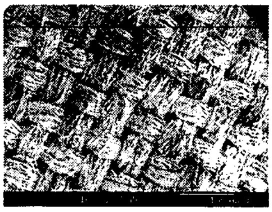
20 % Pt/C



60 % Pt-Ru/C

GAS DIFFUSION LAYER

Carbon cloth



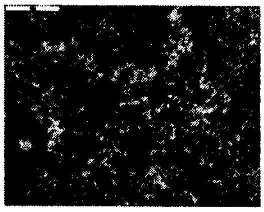
Carbon paper

- Electrode consists of Gas diffusion layer, Catalyst, Binder

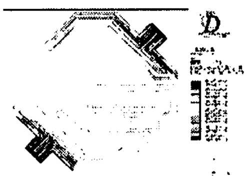
- Gas Diffusion Layer

Porous conductive carbon-based materials such as carbon cloth and carbon paper with a layer of carbon powder bonded to it

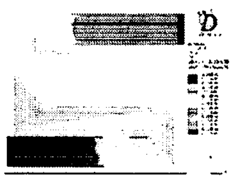
Carbon powder



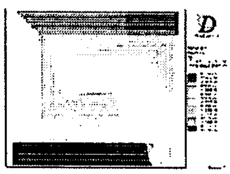
FLOW FIELD TYPES



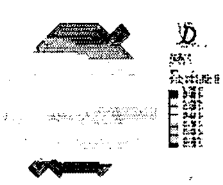
Ballard Power System (공기판)



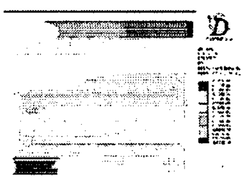
Parallel Serpentine Type (공기판)



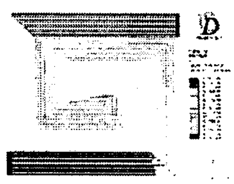
Spiral Type (공기판)



Ballard Power System (수소판)



Parallel Serpentine Type (수소판)

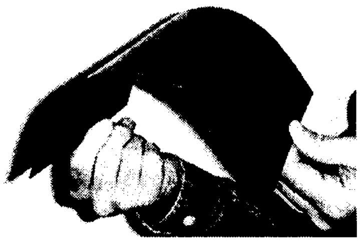


Spiral Type (수소판)

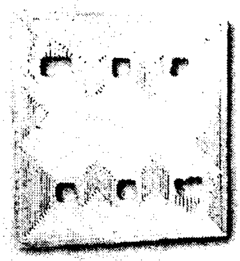
FLOW FIELD MATERIALS

- ➢ Graphite
- ➢ Stainless steel
- ➢ Polymer composites

- ➢ Micro machining
- ➢ Dry etching
- ➢ Molding

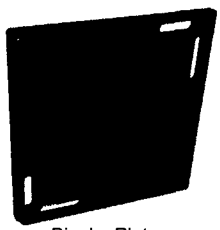


Nissinbo, Japan, flexible graphite, 250 μm



Graftech Inc's flexible graphite for Ballard Mark 901

FUEL CELL STACK



Bipolar Plate

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MEA

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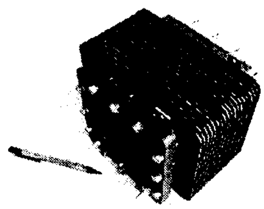
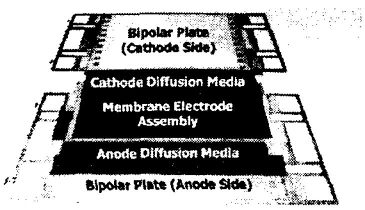
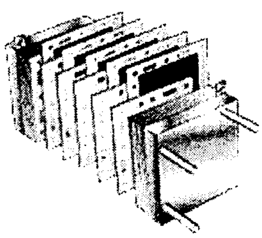


20 cell, 300W PEM, H_2/air, PSI





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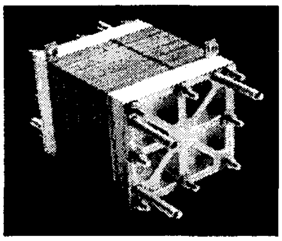
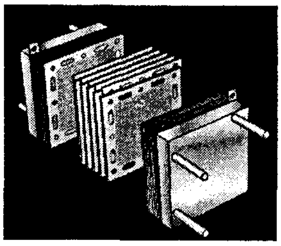
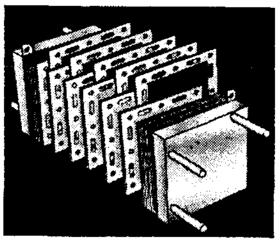
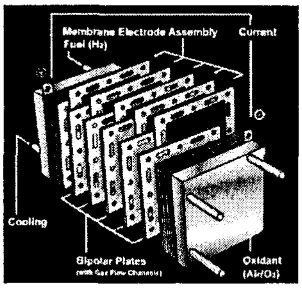
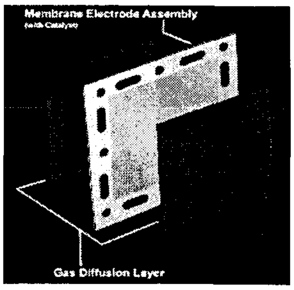
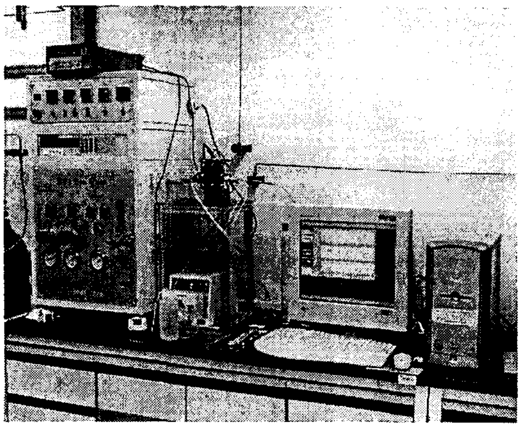
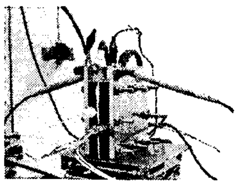
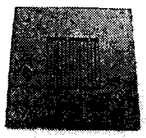
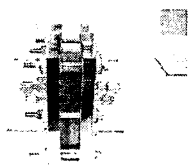







FUEL CELL TEST STATION

FUEL CELLS: The Disruptive Technology

Disruptive technologies typically enable new markets to emergy...companies entering these emerging markets early have significant first-mover advantages

-Clayton Christensen, Harvard Business School-